

IDENTIFICATION OF IRON-BEARING PHASES ON THE MARTIAN SURFACE AND IN MARTIAN METEORITES AND ANALOGUE SAMPLES BY MÖSSBAUER SPECTROSCOPY. R. V. Morris, G. Klingelhöfer, D. G. Agresti, C. Schröder, D. Rodionov, A. Yen, D. Ming, and the Athena Science Team.

Introduction. The Mössbauer spectrometers on the Mars Exploration Rovers (MER) Spirit (Gusev Crater) and Opportunity (Meridiani Planum) have each analyzed more than 100 targets during their ongoing missions (>1050 sols). Here we summarize the Fe-bearing phases identified to date and compare the results to Mössbauer analyses of martian meteorites and lunar samples. We use lunar samples as martian analogues because some, particularly the low-Ti Apollo 15 mare basalts, have bulk chemical compositions that are comparable to basaltic martian meteorites [1,2]. The lunar samples also provide a way to study pigeonite-rich samples. Pigeonite is a pyroxene that is not common in terrestrial basalts, but does often occur on the Moon and is present in basaltic martian meteorites [3,4,5].

Results and Discussion. The Mössbauer parameters IS (isomer shift) and QS (quadrupole splitting) for doublet spectra and IS, QS, and B_{hf} (hyperfine field strength) for sextet spectra are sensitive to the speciation of Fe (oxidation, coordination, and mineralogical states). In Figs. 1 and 2 are the current doublet and sextet identification diagrams, respectively (modified after [6,7]). A total of 13 Fe-bearing phases are identified: Fe^{2+} in olivine, pyroxene, and ilmenite; Fe^{2+} and Fe^{3+} in magnetite and chromite; Fe^{3+} in nanophase ferric oxide, hematite, goethite, jarosite, a Fe^{3+} sulfate (Fe_3D_2), and an unassigned Fe^{3+} phase (Fe_3D_3) associated with jarosite; Fe^0 in metallic Fe-Ni (kamacite); and an unassigned phase whose oxidation state is uncertain ($Fe?D1$; low-spin Fe^{2+} or Fe^{3+}). The average values of their Mössbauer parameters are summarized in Tables 1 and 2. Chromite and $Fe?D1$ have been detected only once. The large envelope for the hematite MB parameters results because the oxide undergoes a magnetic transition (the Morin transition) within the martian diurnal temperature cycle (~190 – 280 K). For well crystalline and chemically pure hematite, this transition occurs at ~250 K.

We have subdivided the pyroxene group of [6,7] into three subgroups (Fig 1a). Subgroup A includes most of the analyses (113 out of 128). Subgroup B (13 analyses) includes rocks from the highly altered Clovis and Independence Classes [6,7,8,9], and Subgroup C (2 analyses) are from rocks in the olivine-rich Algonquin Class. We obtained Mössbauer spectra on martian meteorites and martian analogues at ambient temperatures in order to understand the nature of the pyroxene in MER Mössbauer spectra.

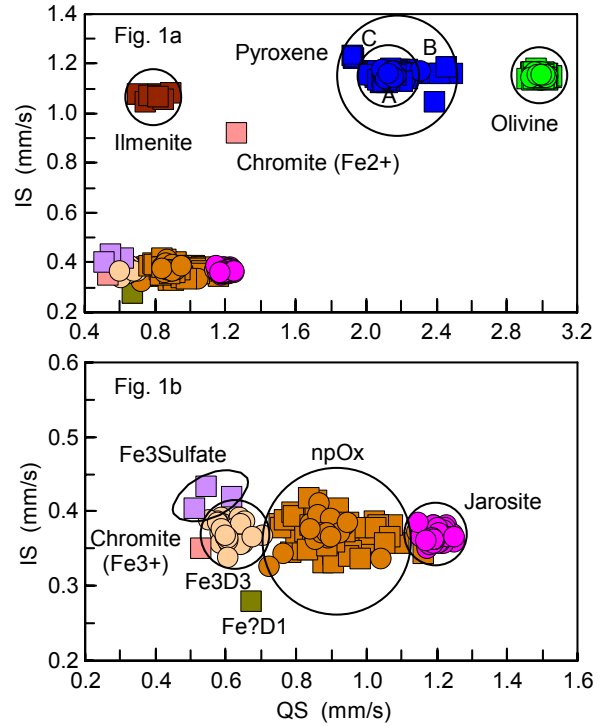


Table 1. Average values and standard deviation of Mössbauer parameters for doublet Fe-bearing phases from Gusev Crater and Meridiani Planum.

Fe Phase ^a	IS (mm/s)	QS (mm/s)	N ^b
Olivine	1.15±0.02	3.00±0.03	92
Pyroxene-A	1.16±0.02	2.13±0.06	113
Pyroxene-B	1.15±0.03	2.30±0.11	13
Pyroxene-C	1.23±0.02	1.92±0.02	2
Ilmenite	1.07±0.02	0.80±0.06	8
npOx	0.37±0.02	0.90±0.09	113
Fe3Sulfate	0.42±0.02	0.56±0.06	3
Jarosite	0.37±0.02	1.20±0.02	56
Fe3D3	0.37±0.02	0.62±0.03	56
Fe?D1 ^c	0.28±0.02	0.67±0.02	1

^a Fe^{2+} and Fe^{3+} in Chromite was inferred in one rock (Assemblee_Grueryer), but the MB parameters were constrained during fitting procedures.

^bNumber of measurements.

^cRock FuzzySmith. Oxidation state uncertain (possibly low-spin Fe^{2+} or oct- Fe^{3+})

In order to make MER and laboratory spectra comparable to each other in terms of data quality, we “degraded” the quality of the laboratory spectra. Mission constraints on time and power do not permit

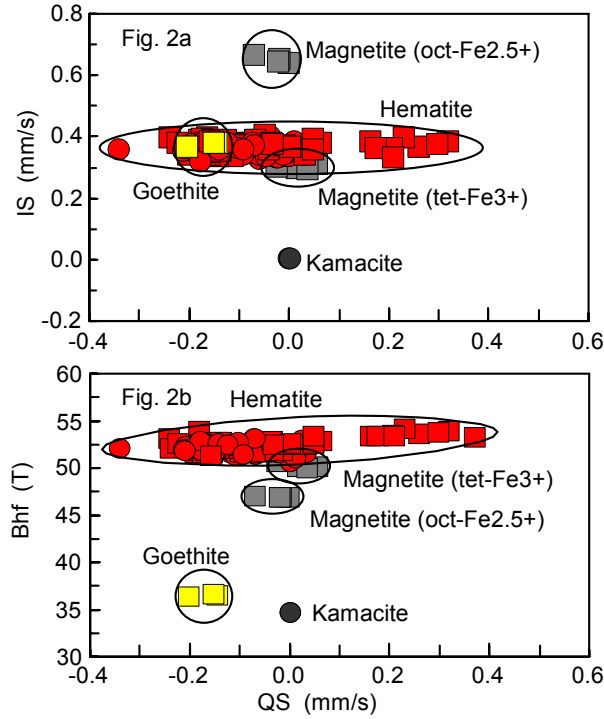


Table 2. Average values and standard deviation of Mössbauer parameters for sextet Fe-bearing phases from Gusev Crater and Meridiani Planum.

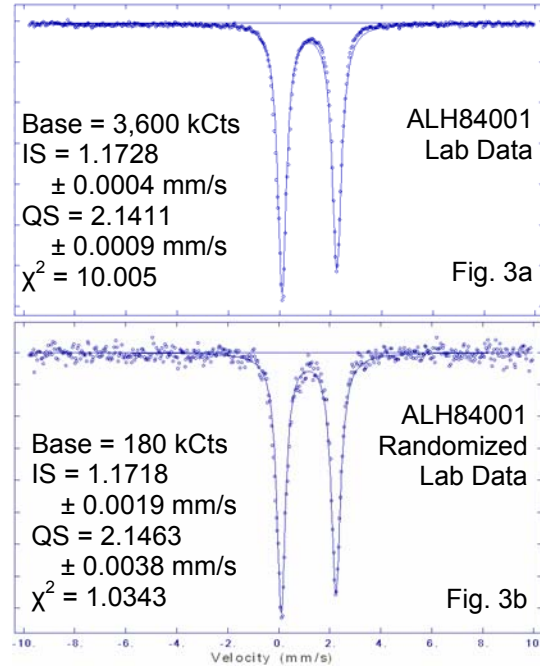
Fe Phase	IS (mm/s)	QS (mm/s)	B _{hf} (T)
Magnetite (4 measurements)			
Oct-Fe ^{2.5+}	0.65±0.02	-0.03±0.03	46.9±0.8
Tet-Fe ³⁺	0.30±0.02	0.02±0.03	50.2±0.8
Goethite (3 measurements)			
Oct-Fe ³⁺	0.38±0.02	-0.17±0.03	35.5±0.8
Hematite (119 measurements)			
Oct-Fe ³⁺	0.37±0.03	-0.3 to 0.4 ^b	50-54 ^b
Kamacite (2 measurements)			
Fe ⁰	0.00±0.02	0.00±0.02	34.7±0.8

^aFe²⁺ and Fe³⁺ in Chromite was inferred in one rock (Assemblee_Grueryer), but the MB parameters were constrained during fitting procedures.

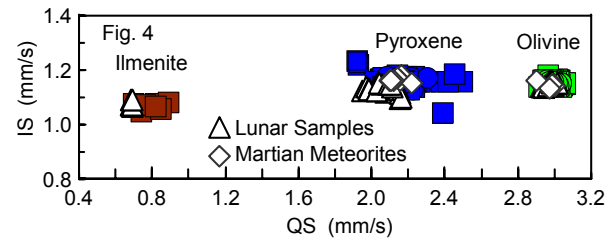
^bWide range results from Morin transition of hematite.

acquiring Mössbauer spectra with arbitrarily good counting statistics. To do this, we developed a computer program called *Randomize* [10]. In Fig. 3, we show the result of applying the procedure to the spectrum of ALH84001. Both spectra were fit with a Lorentzian doublet. The important observation is that an adequate fit was obtained with the MER-like spectrum ($\chi^2 = 1.03$ per degree of freedom) while a much poorer fit ($\chi^2 \sim 10$ per degree of freedom) was obtained with the unaltered laboratory spectrum. However, the values of IS and QS did not change

within statistical error. We are currently using the same procedure on more complex spectra.



In Figure 4, we show doublet Mössbauer parameters for olivine, pyroxene, and ilmenite for martian meteorite, lunar, and MER samples. The important observation is that MER pyroxene-A is mineralogically similar to the pyroxene in lunar and martian meteorite samples. Similarly, pyroxene-B and pyroxene-C are either not represent by those samples or, possibly, are not actually pyroxene.



References. [1] Lodders (1998), *Meteorit. Planet. Sci.*, 33, A183. [2] Lofgren and Lofgren (1981), Cat. Lunar Mare Basalts >40 Grams, LPI Cont. 438. [3] Basaltic Volcanism Study Project (1981). [4] McSween (1994), *Meteoritics*, 29, 757. [5] McSween (1985) *Rev. Geophys.*, 23, 391. [6] Morris et al. (2006), *JGR*, 111, E02S13, doi:10.1029/2005JE002584. [7] Morris et al. (2006) *JGR*, 111, E12S15, doi:10.1029/2006JE002791. [8] Ming et al. (2006), *III*, E02S12, doi:10.1029/2005JE002560. [9] Clark et al. (2007), *JGR*, in press. [10] Agresti and Belton (1974) *Nuc. Inst. Meth.*, 121, 407.